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REGULAR ARTICLE

Application of renormalized coupled-cluster methods to potential function of water

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Abstract The goal of this paper is to examine the performance of the conventional and renormalized single-reference coupled-cluster (CC) methods in calculations of the potential energy surface of the water molecule. A comparison with the results of the internally contracted multi-reference configuration interaction calculations including the quasi-degenerate Davidson correction (MRCI(Q)) and the spectroscopically accurate potential energy surface of water resulting from the use of the energy switching (ES) approach indicates that the relatively inexpensive completely renormalized (CR) CC methods with singles (S), doubles (D), and a non-iterative treatment of triples (T) or triples and quadruples (TQ), such as CR-CCSD(T), CR-CCSD(TQ), and the recently developed rigorously size extensive extension of CR-CCSD(T), termed CR-CC(2,3), provide substantial improvements in the results of conventional CCSD(T) and CCSD(TQ) calculations at larger internuclear separations. It is shown that the CR-CC(2,3) results corrected for the effect of quadruply excited clusters through the CR-CC(2,3)+Q approach can compete with the highly accurate MRCI(Q) data. The excellent agreement between the CR-CC(2,3)+Q and MRCI(Q) results suggests ways of improving the global potential energy surface of water resulting from the use of the ES approach in the regions of intermediate bond stretches and intermediate energies connecting the region of the global minimum with the asymptotic regions.

Keywords Coupled-cluster theory · Renormalized coupled-cluster methods · Potential energy surfaces · Potential function of water

1 Introduction

The key to a successful description of molecular potential energy surfaces involving bond making and breaking is an accurate and balanced treatment of dynamical and non-dynamical electron correlation effects. Balancing dynamical and non-dynamical correlation effects in molecular systems in a proper manner has been one of the main themes of the research conducted by Professor Mark S. Gordon, as reflected, for example, in a large number of truly inspiring computational studies of reaction pathways and mechanisms in various areas of chemistry, carried out over the years by Professor Mark S. Gordon and co-workers. In this paper, we focus on the problem of balancing dynamical and non-dynamical correlations in coupled-cluster (CC) theory [1–5] (cf. Refs. [6–14] for selected reviews).

Conventional single-reference CC methods, such as, for example, the popular CCSD(T) approach [15], in which a non-iterative correction due to triply excited clusters (T) is added to the CCSD (CC singles and doubles) [16–18] energy, and its extensions to quadruply excited clusters (Q) through the CCSD(TQ$_f$) [19], CCSD(TQ),b [20], and similar schemes, provide an excellent description of dynamical correlation effects, which dominate electron correlations in the

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closed-shell regions of potential energy surfaces, but they completely fail when the bond breaking, biradicals, and other situations characterized by larger non-dynamical correlation effects are studied (see, e.g., Refs. [7,10–14,20–57] for representative examples). Traditionally, the adequate treatment of ground- and excited-state potential energy surfaces along bond breaking coordinates and other cases of electronic quasi-degeneracies has been the domain of expert multi-reference methods, and a great deal of progress has been achieved in the area of multi-reference calculations, but even the most successful multi-reference approaches are not without limitations. For example, the low-order multi-reference perturbation theory (MRPT) methods (cf., e.g., Refs. [58,59], and references therein), such as the popular second-order CASPT2 approach [60–63], may encounter serious difficulties with balancing dynamical and non-dynamical correlations in studies of chemical reaction pathways and relative energetics of systems characterized by a varying degree of biradical character [49,50,64], while the more robust multi-reference configuration interaction (MRCI) approaches, including the highly successful internally contracted MRCI approach with quasi-degenerate Davidson corrections (the MRCI(Q) method [65,66]), are often prohibitively expensive. One should also keep in mind that all multi-reference theories require that the user specifies several additional parameters that do not enter single-reference calculations, such as active orbitals or multiple reference determinants and, particularly in the case of MRCI, numerical thresholds for neglecting unimportant electron configurations. At present, a universally applicable and accepted methodology for choosing these parameters is absent [67,68], and a great deal of expertise and experience is required to perform multi-reference calculations in a proper manner (cf., e.g., Ref. [58]).

From this point of view, the development of practical single-reference procedures that could be applied to at least some of the most frequent multi-reference situations, such as single and double bond dissociations, biradicals, and excited states dominated by two-electron transitions, and that could provide a balanced description of dynamical and non-dynamical correlation effects with a more or less black-box effort would be an important step toward widespread progress. This is not to diminish the role of multi-reference approaches, which clearly have the much desired flexibility needed for the accurate treatment of all kinds of electronic quasi-degeneracies. We are only reflecting on the fact that single-reference methods are computational black-boxes, which are generally much easier to use when compared to multi-reference approaches and which have significantly contributed to the popularity of the computational quantum chemistry techniques. Thus, it is useful to explore the possibility of attempting to solve at least some classes of chemical problems involving larger non-dynamical correlation effects without resorting to multi-reference calculations. This has been the motivation behind the recent development of the non-iterative CC approaches based on the partitioning of the similarity-transformed Hamiltonian pursued by Head-Gordon and co-workers [52–56] (cf., also, Ref. [69]), adopted in a slightly modified form by Hirata et al. [38,70] and commonly labeled as the CCSD(2) approximations, the spin-flip CC methods developed by Krylov and co-workers [71–73], the iterative and non-iterative methods [12,13,39,55,56,74–76] based on the extended CC theories of Arponen and Bishop [77–83] and Piecuch and Bartlett [84], and the renormalized and other CC approaches based on the method of moments of CC equations [10–14,20,29,30,35,36,39–42,44,76,85–88], including those that have been incorporated (cf., e.g., Refs. [41,87,89]) in the GAMESS package [90], maintained and distributed at no cost by Professor Mark S. Gordon and Dr. Michael W. Schmidt.

In this work, we focus on the renormalized CC methods for ground electronic states [10–14,20,29,30,39–42,44], which represent a new generation of non-iterative single-reference CC approaches that are designed to improve the results of the CCSD(T) and CCSD(TQ) calculations in the bond breaking/biradical regions of molecular potential energy surfaces, while preserving the ease-of-use (black-box character) and the relatively low computer costs of the CCSD(T) and CCSD(TQ) approximations. In addition to the original and well-established CR-CCSD(T) (completely renormalized CCSD(T)) method [10–13,20,29,30], in which a simple non-iterative correction due to triply excited clusters is added to the CCSD energy, and its CR-CCSD(TQ) (completely renormalized CCSD(TQ)) extensions abbreviated as CR-CCSD(TQ),a and CR-CCSD(TQ),b, and described in Refs. [10–13,20,29,30] as well, in which corrections due to triply and quadruply excited clusters are added to the CCSD energy, we examine the performance of the recently developed rigorously size extensive generalization of CR-CCSD(T), termed CR-CC(2,3), and its augmented CR-CC(2,3)+Q(a) and CR-CC(2,3)+Q(b) versions. The CR-CC(2,3) approach, in which the CCSD energy is corrected for triples in a manner similar to the CCSD(T), CR-CCSD(T), and other non-iterative triples approximations, has been described in detail in Refs. [41,42,44]. In the CR-CC(2,3)+Q(a) and CR-CC(2,3)+Q(b) methods, the CR-CC(2,3) energies are approximately corrected for the dominant quadruples effects, estimated by forming the differences of the CR-CCSD(TQ),a (the CR-CC(2,3)+Q(a) case) or CR-CCSD(TQ),b (the CR-CC(2,3)+Q(b) case) and CR-CCSD(T) energies. Thus, the CR-CC(2,3)+Q(x), x = a, b, energies are calculated as CR-CC(2,3)+Q(x) = CR-CC(2,3) + [CR-CCSD(TQ), x - CR-CCSD(T)] (cf., e.g., Refs. [49,50]). We consider two variants of the CR-CC(2,3) approach, namely, the full CR-CC(2,3) method, as described in Refs. [41,42,44], and the approximate

CR-CC(2,3),A variant, in which the diagonal matrix elements of the similarity-transformed Hamiltonian of CCSD involving triply excited determinants, $\langle \Phi_{ijk}^{abc} | \bar{H}^{(\mathrm{CCSD})} | \Phi_{ijk}^{abc} \rangle$, which enter the CR-CC(2,3) triples correction, are replaced by the spin-orbital energy differences characterizing triple excitations, $(\epsilon_a+\epsilon_b+\epsilon_c-\epsilon_i-\epsilon_j-\epsilon_k)$, where ϵ_p are the usual spin-orbital energies (see, e.g., Ref. [44]). It is interesting to examine the full implementation of CR-CC(2,3) as well as its approximate CR-CC(2,3),A version, since the CR-CC(2,3),A approach is equivalent to the CCSD(2)$_T$ method of Ref. [38], which also aims at eliminating or reducing the failures of CCSD(T) at larger internuclear separations (see Refs. [41,42,44] for further details). The complete list of all CC methods used in this work, papers in which these methods were introduced and described, and scalings of the most expensive CPU steps characterizing each CC method employed in this study with the numbers of occupied and unoccupied orbitals in a molecular basis set used in correlated calculations, n_o and n_u, respectively, are summarized in Table 1.

It has been demonstrated that the CR-CCSD(T) and CR-CC(2,3) approaches (particularly, CR-CC(2,3)) provide very good results for single bond breaking [10–13,29–31,33,34,37,40–44,89,91,92], and reaction pathways involving biradicals and similar cases of electronic quasi-degeneracies [42,46–51,59,93,94], eliminating the failures of the conventional CCSD(T) and CCSD(TQ) methods in those multi-reference situations. The CR-CCSD(TQ),a and CR-CCSD(TQ),b extensions of CR-CCSD(T) provide further improvements in the results for single bond breaking [11–13,29,31,33], while helping to obtain reasonable accuracies in cases of multiple bond stretching or breaking [11–13,20,28–30,36,39–41,44,76] (cf., also, Ref. [57] for the analogous findings for the approximate versions of CR-CCSD(TQ)). However, with an exception of one study of a global potential energy surface of the BeFH system [37], none of the previous calculations have examined the performance of the CR-CC approaches in large-basis-set calculations for different potential energy surface cuts of a triatomic molecule. This is particularly true for the recently developed [41,42,44] CR-CC(2,3) approach. According to the benchmark calculations reported in Refs. [41,42,44] and several applications to reaction mechanisms in organic [42,51] and bioinorganic [49,50] chemistries, the CR-CC(2,3) approach provides the results which are competitive or at least as good as those obtained with CCSD(T) for closed-shell molecules near the equilibrium geometries, while improving the already reasonable results of the CR-CCSD(T) calculations in the biradical/bond breaking regions. Moreover, the CR-CC(2,3) approach appears to be substantially more accurate than another type of renormalized CC approach, termed LR-CCSD(T) [40,95], and the aforementioned CCSD(2)$_T$ [38] method [41,42,44].

Table 1 The list of CC methods used in this work, papers in which these methods were introduced, and scalings of the most expensive CPU steps characterizing each method with the numbers of occupied (n_o) and unoccupied (n_u) orbitals in a molecular basis set used in correlated calculations

Method	Reference(s)	The most expensive CPU steps	
		Iterative	Non-iterative
CCSD[a]	[16–18]	$n_o^2n_u^4$	
CCSD(T)	[15]	$n_o^2n_u^4$	$n_o^3n_u^4$
CR-CCSD(T)	[10,30]	$n_o^2n_u^4$	$2n_o^3n_u^4$
CR-CC(2, 3), A $\equiv$ CCSD(2)$_T$[b]	[38,41,42,44]	$n_o^2n_u^4$	$2n_o^3n_u^4$
CR-CC(2,3)[c]	[41,42,44]	$n_o^2n_u^4$	$2n_o^3n_u^4$
CCSD(TQ),b[d]	[20]	$n_o^2n_u^4$	$n_o^3n_u^4$ (T), $n_o^2n_u^5$ (Q)
CR-CCSD(TQ),x (x = a, b)[e]	[20]	$n_o^2n_u^4$	$2n_o^3n_u^4$ (T), $2n_o^2n_u^5$ (Q)
CR-CC(2,3)+Q(x) (x = a, b)[f]		$n_o^2n_u^4$	$2n_o^3n_u^4$ (T), $2n_o^2n_u^5$ (Q)

[a] Reference [16] describes the spin-orbital formulation of CCSD. For the non-orthogonally spin-adapted formulation of CCSD for singlet states, see Ref. [17]. For the orthogonally spin-adapted CCSD theory for singlet states, see Ref. [18]

[b] CCSD(2)$_T$ is obtained by neglecting contributions due to connected quadruply excited clusters in the CCSD(2) method of Ref. [70]. It can also be obtained from the full CR-CC(2,3) approach of Refs. [41,42] by replacing the diagonal matrix elements of the similarity-transformed Hamiltonian of CCSD involving triply excited determinants, $\langle \Phi_{ijk}^{abc} | \bar{H}^{(\mathrm{CCSD})} | \Phi_{ijk}^{abc} \rangle$, which enter the CR-CC(2,3) triples correction, by the spin-orbital energy differences characterizing triple excitations, $(\epsilon_a+\epsilon_b+\epsilon_c-\epsilon_i-\epsilon_j-\epsilon_k)$, where ϵ_p are the usual spin-orbital energies [44]

[c] The full CR-CC(2,3) approach, also referred to in Refs. [41,44] as variant D of the CR-CC(2,3) or CR-CCSD(T)$_{\mathcal{L}}$ method

[d] CCSD(TQ),b can be obtained from the factorized CCSD(TQ$_\mathrm{f}$) approach of Ref. [19] by replacing the first-order estimate for the doubly excited T_2 clusters in the correction due to quadruples defining the CCSD(TQ$_\mathrm{f}$) energy by the CCSD value of T_2

[e] CR-CCSD(TQ),a is equivalent to the CR-CCSD(TQ) approach defined in Refs. [10,30]. CR-CCSD(TQ),b is obtained from CR-CCSD(TQ),a by replacing the first-order estimate for the doubly excited T_2 clusters in the correction due to quadruples defining the CR-CCSD(TQ),a energy by the CCSD value of T_2

[f] CR-CC(2, 3)+Q(x) = CR-CC(2, 3) + [CR-CCSD(TQ), x − CR-CCSD(T)], x = a, b

As shown in Refs. [41,42,44], the CR-CC(2,3) theory seems to provide the results of the full CCSDT (CC singles, doubles, and triples) [96,97] quality when bond breaking is examined. It is, therefore, very interesting to investigate how the CR-CC(2,3) approach performs when a few different potential energy surface cuts of a triatomic molecule are examined. As explained in Refs. [41,42], the CR-CC(2,3) approach can be extended to quadruple excitations through the CR-CC(2,4) theory, but the CR-CC(2,4) method has not been implemented yet and we may have to investigate formal issues such as the coupling of triples and quadruples in the definition of the CR-CC(2,4) energy corrections, ignored in the original papers on the CR-CC(m_A,m_B) methods [41,42]. On the other hand, a highly accurate description of potential energy surfaces that might help various spectroscopic and dynamical studies may require the inclusion of quadruples, in addition to triples that are already well described by the CR-CC(2,3) theory. Thus, in this paper we examine the effect of quadruples on the CR-CC(2,3) results by adding the *a posteriori* corrections due to quadruply excited clusters extracted, as explained above, from the CR-CCSD(TQ),a or CR-CCSD(TQ),b calculations, to the CR-CC(2,3) energies.

The CR-CCSD(T), CR-CCSD(TQ),a, CR-CCSD(TQ),b, CR-CC(2,3),A $\equiv$ CCSD(2)$_T$, CR-CC(2,3), CR-CC(2,3)+Q(a), and CR-CC(2,3)+Q(b) methods, and their conventional (i.e., not renormalized) CCSD(T) and CCSD(TQ),b analogs are carefully tested by examining three important cuts of the global potential energy surface of the water molecule. Those cuts are: (i) the dissociation of a single O–H bond which correlates with the H($1s\ ^2S$) + OH($X\ ^2\Pi$) asymptote, (ii) the simultaneous dissociation of both O–H bonds of the water molecule correlating with the 2H($1s\ ^2S$) + O($2p^4\ ^3P$) channel, and (iii) the C_{2v} dissociation pathway of the water molecule into $H_2(X\ ^1\Sigma_g^+)$ and O($2p^4\ ^1D$). The CR-CCSD(T), CR-CCSD(TQ),a, CR-CCSD(TQ),b, CR-CC(2,3),A, CR-CC(2,3), CR-CC(2,3)+Q(a), and CR-CC(2,3)+Q(b) results and the corresponding CCSD, CCSD(T), and CCSD(TQ),b results, all obtained with the basis sets of the aug-cc-pCVXZ (X = D, T, Q) quality [98–101], are compared with the results of the large-scale MRCI(Q) calculations, also carried out in this work, and the spectroscopically accurate global potential energy surface of water resulting from the use of the energy switching (ES) approach [102].

We chose the water molecule as our benchmark system for a number of reasons. Clearly, water is among the most important molecules and a prototype system for a variety of spectroscopic and reaction dynamics studies. There are many applications involving water molecule in which the knowledge of a reliable potential energy surface is required. Selected examples of such applications include the spectrum of the water vapor, which is important for the understanding of the absorption and retention of sunlight in Earth's atmosphere and physics of other planets and stars [103–112], and combustion studies involving hot steam. For example, the O($2p^4\ ^1D$) + $H_2(X\ ^1\Sigma_g^+)$ $\rightarrow$ OH($X\ ^2\Pi$) + H($1s\ ^2S$) reaction, which takes place on the ground-state potential energy surface of water, is known to play a significant role in combustion and atmospheric chemistry [113,114]. Two of the dissociation pathways examined in this work, namely, the dissociation of a single O–H bond and the C_{2v} dissociation path of the water molecule into $H_2(X\ ^1\Sigma_g^+)$ and O($2p^4\ ^1D$) are directly related to this important reaction. The water molecule has received considerable attention in recent years due to several attempts to produce the spectroscopically and dynamically accurate global potential energy surface using *ab initio* and other theoretical means [102,109,115–119]. One such attempt has resulted in the ES potential function used in this work [102]. By comparing various CR-CC and MRCI(Q) data with the energies provided by the ES potential function, we may suggest ways of improving the ES and similar potentials in intermediate-energy regions where no precise or well understood spectroscopic or ab initio data are available. Thus, in addition to testing CR-CC methods, we may contribute to the ongoing effort to produce the high accuracy water surface which could be used in a variety of spectroscopic and dynamical applications.

2 Computational details

In order to illustrate the performance of the renormalized CC methods discussed in the Introduction and listed in Table 1, we performed the CR-CCSD(T), CR-CCSD(TQ),a, CR-CCSD(TQ),b, CR-CC(2,3),A (= CCSD(2)$_T$), CR-CC(2,3), CR-CC(2,3)+Q(a), and CR-CC(2,3)+Q(b) calculations for the three cuts of the global potential energy surface of the water molecule. Those cuts are: (i) the dissociation of a single O–H bond, which correlates with the H($1s\ ^2S$) + OH($X\ ^2\Pi$) asymptote, (ii) the simultaneous dissociation of both O–H bonds, which correlates with the 2H($1s\ ^2S$) + O($2p^4\ ^3P$) channel, and (iii) the C_{2v} dissociation pathway of the water molecule into $H_2(X\ ^1\Sigma_g^+)$ and O($2p^4\ ^1D$). In the case of cut (i), one of the two O–H bonds and the H–O–H angle were kept fixed at their respective equilibrium values taken from Ref. [109] (R_e = 0.95785 Å and α_e = 104.501 degree, respectively). In the case of the C_{2v}-symmetric cut (ii), the H–O–H angle α was kept fixed at its equilibrium value taken from Ref. [109] (α_e = 104.501 degree). In the case of another C_{2v}-symmetric cut, namely cut (iii), we followed the approximate energy path toward the dissociation of the water molecule into $H_2(X\ ^1\Sigma_g^+)$ and O($2p^4\ ^1D$), determined using the potential function of Ref. [102] and defined by the coordinate Y, which is the distance between the O nucleus and the line connecting the H nuclei, and the properly optimized H–O–H angle α [113,114]. The equilibrium values of Y and α are Y_e = 0.58641 Å and

$\alpha_e = 104.501$ degree. The results of various CR-CC calculations are compared with those obtained with the conventional CCSD, CCSD(T), and CCSD(TQ),b methods, which are very well suited for the equilibrium region but are expected to face considerable difficulties when water starts to dissociate into open-shell fragments, and with the results obtained with the MRCI(Q) approach, which is capable of providing an accurate global potential energy surface, including all three dissociation channels listed above.

We also compare the results of various CR-CC and MRCI(Q) calculations with the highly accurate global potential energy surface of water resulting from the use of the ES approach of Varandas [102]. The ES surface of Ref. [102] was obtained by combining and further refining the many-body expansion [120] potential of Murrell and Carter [115] and the polynomial potential form of Polyansky, Jensen, and Tennyson [116]. The ES surface has a spectroscopic or nearly spectroscopic ($\sim$1–10 cm^{-1}) accuracy up to about 19,000 cm^{-1} above the global minimum and remains quite accurate at higher energies. With the proper treatment of long-range forces and other suitable refinements, the ES potential of Ref. [102] has an overall double many-body expansion [121–124] quality, making it very useful to study reaction dynamics involving water. In particular, the ES potential of Ref. [102] used in this work, and its multi-sheeted extensions [118, 119], have been exploited in a number of dynamical calculations, including, for example, the successful rate constant and cross-section calculations for the $O(2p^4\ ^1D) + H_2(X\ ^1\Sigma_g^+)$ reaction [113,114]. As mentioned in the Introduction, the $O(2p^4\ ^1D) + H_2(X\ ^1\Sigma_g^+) \rightarrow OH(X\ ^2\Pi) + H(1s\ ^2S)$ reaction, which takes place on the ground-state potential energy surface of water, is known to play a significant role in combustion and atmospheric chemistry. Two of the above cuts (cut (i) and (iii)) are directly related to this process. In addition to testing the CR-CC (also, MRCI(Q)) methods, by comparing the best CR-CC and MRCI(Q) data with the energies provided by the ES potential function, we suggest ways of improving the ES potential, particularly in intermediate and selected higher-energy regions where precise or well understood spectroscopic data are not always available and where, as shown in this work, the best CR-CC and MRCI(Q) calculations almost perfectly agree with each other.

All CC and CR-CC calculations were performed using the spin- and symmetry-adapted restricted Hartree–Fock (RHF) determinant as a reference. The MRCI(Q) calculations were performed using the usual multi-determinantal reference obtained in the single-root complete-active-space self-consistent-field (CASSCF) calculations. The active space used in the CASSCF and subsequent MRCI(Q) calculations consisted of six valence orbitals that correlate with the $1s$ shells of the hydrogen atoms and the $2s$ and $2p$ shells of the oxygen atom. In analogy to active orbitals, the lowest-energy molecular orbital ($\sim$1s orbital of oxygen) was optimized in CASSCF calculations, but unlike active orbitals that change occupancies it remained doubly occupied in all reference determinants defining the CASSCF and MRCI(Q) wave functions. Since our ab initio results are compared with the spectroscopically accurate ES surface of Ref. [102] and since it is well known that core electrons can significantly affect energy differences between different points on the potential energy surface, including the water potential [109,117,125], all electrons were correlated in the CC, CR-CC, and CASSCF-based MRCI(Q) calculations. This distinguishes our calculations from Refs. [109,125], in which the effects of core electrons were added as the a posteriori corrections to the results of valence-electron calculations.

The calculations were performed with the aug-cc-pCVXZ basis sets with $X = $ D, T, Q [98–101], in which additional tight functions are added to the valence basis sets of the aug-cc-pVXZ quality to improve the description of core and core-valence correlation effects. The CCSD, CCSD(T), CCSD(TQ),b, CR-CCSD(T), CR-CCSD(TQ),a, CR-CCSD(TQ),b, CR-CC(2,3),A, CR-CC(2,3), CR-CC(2,3)+Q(a), and CR-CC(2,3)+Q(b) calculations were performed with the system of CC/CR-CC computer codes described in Refs. [20,30,41,89] and incorporated in the GAMESS package [90]. The MRCI(Q) calculations were performed with the MOLPRO package [126]. In addition to the series of MRCI(Q) calculations using the aug-cc-pCVXZ basis sets with $X = $ D, T, Q, we performed the high accuracy MRCI(Q) calculations using the aug-cc-pCV5Z basis, to determine if the aug-cc-pCVQZ results are reasonably well converged. We could not perform such calculations using the CC and CR-CC methods, since the atomic integral package used by GAMESS is restricted to g functions and the aug-cc-pCV5Z basis contains h functions which we did not want to drop in an ad hoc manner. Fortunately, we do not observe substantial changes in the results, when going from the aug-cc-pCVQZ to aug-cc-pCV5Z basis sets, which could alter our main conclusions. In order to facilitate our presentation, we refer to the aug-cc-pCVXZ basis set by mentioning the value of it's cardinal number X ($X = 2$ for aug-cc-pCVDZ, $X = 3$ for aug-cc-pCVTZ, $X = 4$ for aug-cc-pCVQZ, and $X = 5$ for aug-cc-pCV5Z). For example, we write "the $X = 3$ basis set" instead of "the aug-cc-pCVTZ basis set." Instead of writing "the CR-CC(2,3) calculations with the aug-cc-pCVTZ basis set," we simply write "the CR-CC(2,3)/$X = 3$ calculations."

3 Numerical results and discussion: probing potential energy surface of the water molecule with the conventional and renormalized coupled-cluster methods

The results of our calculations are summarized in Tables 2 to 9. Table 2 serves as a reference for the remaining tables,

Table 2 The ES and MRCI(Q) energies for the three potential energy surface cuts of water examined in this study: (i) the dissociation of a single O–H bond, (ii) the C_{2v}-symmetric dissociation of both O–H bonds, and (iii) the C_{2v} dissociation into $H_2(X\ ^1\Sigma_g^+)$ and $O(2p^4\ ^1D)$

R	α	ES	MRCI(Q)			
			$X=2$	$X=3$	$X=4$	$X=5$
$H_2O(\tilde{X}\ ^1A_1) \rightarrow H(1s\ ^2S) + OH(X\ ^2\Pi)$						
$1.25R_e$	104.501	7367	6753	7177	7354	7396
$1.50R_e$	104.501	18862	17945	18733	18990	19059
$1.75R_e$	104.501	28857	27478	28510	28838	28928
$2.00R_e$	104.501	35583	34067	35226	35615	35721
$2.50R_e$	104.501	41024	40030	41277	41736	41857
$3.00R_e$	104.501	42816	41521	42811	43282	43407
$4.00R_e$	104.501	43779	41938	43250	43723	43848
$5.00R_e$	104.501	43887	41970	43281	43754	43879
$H_2O(\tilde{X}\ ^1A_1) \rightarrow 2H(1s\ ^2S) + O(2p^4\ ^3P)$						
$1.25R_e$	104.501	14366	13119	14027	14380	14464
$1.50R_e$	104.501	36152	34506	36188	36706	36843
$1.75R_e$	104.501	54629	52359	54555	55224	55407
$2.00R_e$	104.501	67354	64408	66912	67730	67950
$2.50R_e$	104.501	78170	74341	77126	78113	78374
$3.00R_e$	104.501	80585	76298	79196	80207	80478
$4.00R_e$	104.501	81191	76792	79732	80752	81020
$5.00R_e$	104.501	81219	76840	79776	80795	81062
Y	α	ES	MRCI(Q)			
			$X=2$	$X=3$	$X=4$	$X=5$
$H_2O(\tilde{X}\ ^1A_1) \rightarrow H_2(X\ ^1\Sigma_g^+) + O(2p^4\ ^1D)$						
0.80	78.808	4998	4501	4809	4981	5023
0.90	69.118	10660	9888	10374	10639	10701
1.00	61.113	17927	16642	17326	17666	17745
1.10	56.072	26589	23953	24887	25287	25383
1.20	53.429	36326	31497	32699	33148	33260
1.30	48.314	43726	38301	39623	40095	40215
1.50	38.432	52137	48794	50171	50662	50786
1.75	29.171	57311	55342	56604	57116	57236
2.00	22.855	58486	56770	57663	58181	58294
4.00	10.589	58696	57534	58058	58590	58694

R is an O–H distance defining the dissociating O–H bond(s), Y (in Å) is the distance between O and the line connecting both H nuclei, and α (in degree) is the H–O–H angle. The equilibrium values of R, Y, and α are $R_e = 0.95785$ Å, $Y_e = 0.58641$ Å, and $\alpha_e = 104.501$ degree [109]. All energies E (in cm^{-1}) are reported as $E - E(R_e, \alpha_e)$, where $E(R_e, \alpha_e)$ are the corresponding values of E at the equilibrium geometry. X is a cardinal number defining the aug-cc-pCVXZ basis sets used in the MRCI(Q) calculations. In all MRCI(Q) calculations, all electrons were correlated

providing the MRCI(Q) and ES energies along the three dissociation pathways considered in our calculations. As one can see, the three potential energy surface cuts probe different energy regions. The single O–H bond dissociation is characterized by the lowest energies (always reported in this work relative to the corresponding energies at the equilibrium geometry of Ref. [109], so that all energies are 0 at the equilibrium geometry), which do not exceed 44,000 cm^{-1}. The C_{2v}-symmetric dissociation pathway that leads to the $H_2(X\ ^1\Sigma_g^+)$ and $O(2p^4\ ^1D)$ products goes to higher energies, on the order of 59,000 cm^{-1}, and the highest energies, on the order of 81,000 cm^{-1}, are reached, when the simultaneous dissociation of both O–H bonds is examined. The results in Table 2 show that the large scale MRCI(Q) calculations with the $X = 5$ basis set agree with the ES potential, to within ~10–200 cm^{-1}, in the $R_e \leq R \leq 2R_e$ and $R \geq 4R_e$ regions of cut (i), $R_e \leq R < 1.5R_e$ and $R \geq 2.5R_e$ regions of cut (ii), and $Y_e \leq Y \leq 1.0$ Å and $Y \geq 1.75$ Å

Table 3 The dissociation of a single O–H bond in water (into H($1s\ ^2S$) + OH($X\ ^2\Pi$); cut(i))

R	CCSD			CCSD(T)			CR-CCSD(T)			CR-CC(2,3),A[a]			CR-CC(2,3)		
	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$
$1.25R_e$	7033	7483	7662	6796	7181	7351	6845	7247	7419	6825	7219	7389	6810	7216	7393
$1.50R_e$	18587	19428	19691	18023	18744	18988	18151	18909	19157	18105	18843	19087	18063	18829	19087
$1.75R_e$	28610	29763	30108	27567	28529	28844	27843	28873	29194	27764	28753	29065	27653	28696	29024
$2.00R_e$	35889	37303	37739	34109	35231	35620	34675	35913	36313	34554	35716	36098	34315	35547	35966
$2.50R_e$	43451	45308	45904	39363	40628	41117	41145	42687	43205	40919	42296	42775	40399	41939	42461
$3.00R_e$	46000	48158	48836	39387	40600	41087	42828	44537	45093	42518	43996	44495	41847	43517	44095
$4.00R_e$	47145	49527	50262	37553	38518	38938	43188	44976	45541	42809	44318	44815	42106	43834	44443
$5.00R_e$	47325	49760	50508	36759	37592	37975	43107	44892	45453	42716	44215	44708	42063	43771	44379

R	CCSD(TQ),b			CR-CCSD(TQ),a			CR-CCSD(TQ),b			CR-CC(2,3)+Q(a)[b]			CR-CC(2,3)+Q(b)[b]		
	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$
$1.25R_e$	6771	7167	7338	6793	7197	7370	6794	7199	7372	6758	7166	7344	6759	7168	7346
$1.50R_e$	17965	18703	18949	18036	18797	19046	18035	18798	19048	17947	18717	18976	17946	18718	18978
$1.75R_e$	27461	28446	28764	27656	28689	29012	27648	28685	29010	27466	28512	28843	27457	28509	28840
$2.00R_e$	33948	35098	35491	34420	35659	36060	34398	35643	36047	34060	35293	35714	34037	35277	35701
$2.50R_e$	39145	40432	40925	40811	42340	42858	40759	42297	42820	40066	41592	42114	40014	41549	42075
$3.00R_e$	39234	40445	40928	42482	44162	44715	42432	44119	44676	41501	43141	43716	41451	43098	43677
$4.00R_e$	37630	38536	38941	42842	44580	45140	42845	44591	45154	41759	43438	44042	41763	43449	44056
$5.00R_e$	36964	37713	38075	42735	44460	45016	42798	44536	45095	41690	43339	43941	41754	43416	44021

One of the two O–H bonds and the H–O–H angle are kept fixed at their respective equilibrium values taken from Ref. [109] ($R_e = 0.95785$ Å and $\alpha_e = 104.501$ degree, respectively). R is an O–H distance defining the dissociating O–H bond. All energies E (in cm^{-1}) are reported as $E - E(R_e, \alpha_e)$, where $E(R_e, \alpha_e)$ are the corresponding values of E at the equilibrium geometry. X is a cardinal number defining the aug-cc-pCVXZ basis sets used in the calculations. In all CC calculations, all electrons were correlated

[a] Equivalent to the CCSD(2)$_T$ approach of Ref. [38]

[b] CR-CC(2, 3)+Q(x) = CR-CC(2, 3) + [CR-CCSD(TQ), x − CR-CCSD(T)], x = a, b

of cut (iii) (R is the O–H separation for the dissociating O–H bond or bonds; the meaning of Y has been explained in Sect. 2). The MRCI(Q)/$X = 4$ results are not much different, producing the results that in most cases do not differ from the MRCI(Q)/$X = 5$ results by more than 100–200 cm^{-1} in the higher energy regions. Thus, with an exception of the region of intermediate R and Y values ($2R_e < R < 4R_e$ for cut (i), $1.5R_e \le R < 2.5R_e$ for cut (ii), and 1.0 Å $< Y <$ 1.75 Å for cut (iii), the MRCI(Q)/$X = 4$ or MRCI(Q)/$X = 5$ and ES potential functions agree very well. Clearly, they cannot perfectly agree, since MRCI(Q) is not the exact theory. Moreover, our MRCI(Q) calculations are the standard non-relativistic calculations, ignoring relativistic, non-adiabatic, and quantum electrodynamical effects which all contribute to the water potential energy surface [109]. Besides, the minimum energy path defining cut (iii) determined from the ES function is certainly not identical to the similar path that would result from the MRCI(Q) calculations and there may be other small differences in the details of the MRCI(Q)/$X = 4$ or MRCI(Q)/$X = 5$ and ES potentials. On the other hand, the differences between the MRCI(Q)/$X = 4$ or MRCI(Q)/$X = 5$ and ES potential energy surfaces in the aforementioned regions of intermediate R and Y values, and intermediate or higher, but not the highest energies, which are as much as 700–800 cm^{-1} for cut (i) in the $R \approx 2.5R_e$ region, 600–800 cm^{-1} for cut (ii) in the $R \approx 1.75R_e$ region, and 3,500–3,600 cm^{-1} for cut (iii) in the $Y \approx 1.3$ Å region, cannot be explained by the mere neglect of the relativistic, non-adiabatic, and quantum electrodynamical effects. They indicate that either the MRCI(Q) approach is insufficiently accurate or the ES potential needs further refinement. The former is always possible, but the latter explanation would not be a complete surprise either, since we must remember that the ES potential function is constructed by combining the many-body expansion potential of Murrell and Carter [115] and the polynomial potential form of Polyansky, Jensen, and Tennyson [116]. This makes the ES potential very accurate around the minimum, up to about 19,000 cm^{-1}, and in the asymptotic regions, including the H($1s\ ^2S$) + OH($X\ ^2\Pi$), 2H($1s\ ^2S$) + O($2p^4\ ^3P$), and $H_2(X\ ^1\Sigma_g^+)$ + O($2p^4\ ^1D$) asymptotes examined in this study, but the accuracy of the ES potential function in the regions of intermediate internuclear separations and energies which connect the spectroscopic and asymptotic regions of the water potential energy

Table 4 The C_{2v}-symmetric double dissociation of water (into $2H(1s\ ^2S) + O(2p^4\ ^3P)$; cut (ii))

R	CCSD			CCSD(T)			CR-CCSD(T)			CR-CC(2,3),A[a]			CR-CC(2,3)		
	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$
$1.25R_e$	13719	14684	15042	13212	14041	14381	13325	14191	14534	13279	14127	14466	13226	14100	14459
$1.50R_e$	35972	37782	38315	34695	36253	36744	35036	36676	37175	34908	36501	36992	34780	36421	36960
$1.75R_e$	55003	57497	58208	52556	54646	55290	53387	55626	56283	53100	55245	55884	52833	55093	55771
$2.00R_e$	68471	71615	72538	64123	66666	67498	66020	68801	69647	65357	67973	68789	64789	67559	68439
$2.50R_e$	79497	84194	85573	67039	70640	71855	75186	79223	80442	72329	75866	77002	71027	74896	76142
$3.00R_e$	79696	85261	86853	56639	59917	61074	74436	79026	80364	69964	73450	74560	68538	72292	73618
$4.00R_e$	78228	84053	85708	43548	45309	46055	72499	77153	78494	67359	70653	71700	66295	69878	71116
$5.00R_e$	77699	83526	85183	39737	40815	41383	71808	76416	77746	66549	69777	70810	65742	69234	70232

R	CCSD(TQ),b			CR-CCSD(TQ),a			CR-CCSD(TQ),b			CR-CC(2,3)+Q(a)[b]			CR-CC(2,3)+Q(b)[b]		
	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$
$1.25R_e$	13157	14010	14351	13208	14079	14424	13212	14085	14430	13109	13988	14349	13113	13993	14355
$1.50R_e$	34552	36146	36641	34749	36395	36897	34752	36403	36908	34493	36139	36682	34496	36148	36693
$1.75R_e$	52314	54437	55086	52907	55144	55804	52892	55142	55806	52352	54611	55293	52338	54608	55295
$2.00R_e$	64074	66549	67364	65481	68219	69059	65469	68208	69053	64250	66976	67851	64238	66965	67845
$2.50R_e$	75356	76491	77198	76337	80006	81153	77686	80953	82021	72177	75679	76853	73526	76626	77722
$3.00R_e$	93104	88747	88276	79038	83153	84401	82900	86370	87477	73140	76418	77654	77003	79635	80730
$4.00R_e$	126095	115610	113773	82241	86600	87911	85748	89689	90907	76037	79325	80533	79544	82415	83529
$5.00R_e$	139384	127204	124945	84989	89436	90773	86028	90109	91361	78923	82253	83260	79962	82926	83848

The H–O–H angle is kept fixed at its equilibrium value taken from Ref. [109] ($\alpha_e = 104.501$ degree). R is an O–H distance and $R_e = 0.95785$ Å is the equilibrium value of R [109]. All energies E (in cm^{-1}) are reported as $E - E(R_e, \alpha_e)$, where $E(R_e, \alpha_e)$ are the corresponding values of E at the equilibrium geometry. X is a cardinal number defining the aug-cc-pCVXZ basis sets used in the calculations. In all CC calculations, all electrons were correlated

[a] Equivalent to the CCSD(2)$_T$ approach of Ref. [38]

[b] CR-CC(2, 3)+Q(x) = CR-CC(2, 3) + [CR-CCSD(TQ), x − CR-CCSD(T)], x = a, b

surface is less certain. A comparison of the MRCI(Q) and best CR-CC data may help us to decide if the ES potential needs further improvements in the regions of intermediate R or Y values and energies that connect the region of the global minimum with the asymptotes.

The main CC and CR-CC results for the three potential energy surface cuts examined in this work (the CC and CR-CC energies calculated relative to the corresponding energies at the minimum taken from Ref. [109]) are given in Tables 3, 4, 5. In order to facilitate our analysis, we give in Tables 6, 7, 8 the differences between the CC/CR-CC and the corresponding MRCI(Q) energies for each of the three aug-cc-pCVXZ basis sets used in the CC/CR-CC calculations. In Table 9, we compare the errors in the best CR-CC(2,3)+Q(b)/$X = 4$ results, relative to the MRCI(Q)/$X = 4$ data, with the differences between the CR-CC(2,3)+Q(b)/$X = 4$ and ES energies and the analogous differences between the MRCI(Q)/$X = 4$, 5 and ES energies.

A close inspection of Tables 3 to 8, particularly Tables 6 to 8, allows us to appreciate the nature of the challenges the single-reference CC methods face when describing global potential energy surfaces along bond breaking coordinates. It also allows us to reemphasize the usefulness of the three dissociation pathways that we chose in this study to test the CC and CR-CC methods, which create different types of bond breaking or bond stretching situations. Indeed, the relatively large differences between the CCSD and MRCI(Q) energies, which exceed ~300–700 cm^{-1} for small stretches of the O–H bond(s) ($R \approx 1.25R_e - 1.5R_e$ in the case of cut (i), $R \approx 1.25R_e$ in the case of cut (ii), and $Y \approx 0.8 - 0.9$ Å in the case of cut (iii)), and huge differences between the CCSD and MRCI(Q) energies, on the order of 4,000–7,000 cm^{-1}, in the $R \geq 3R_e$ region of cut (i) and $R \approx 2R_e - 3R_e$ region of cut (ii), and more than 1,000 cm^{-1} for larger Y values in the case of cut (iii), clearly show that one needs to include higher-than-doubly excited clusters in the CC calculations to obtain reasonable results. Not surprisingly, the CCSD approach is qualitatively correct in the case of cut (i), which corresponds to single-bond breaking (which is, in the zero-order approximation, a two-electron process), producing errors relative to MRCI(Q) which monotonically increase with R, while being completely erratic in the case of the double O–H dissociation defining cut (ii), producing a large hump in the region of intermediate R values. The CCSD

Table 5 The C_{2v} dissociation of water into $H_2(X\ ^1\Sigma_g^+)$ and $O(2p^4\ ^1D)$ (cut (iii))

Y	α	CCSD			CCSD(T)			CR-CCSD(T)			CR-CC(2,3),A[a]			CR-CC(2,3)		
		$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$
0.80	78.808	4774	5126	5303	4555	4847	5017	4597	4904	5074	4579	4880	5049	4558	4867	5044
0.90	69.118	10376	10928	11201	9977	10432	10691	10056	10536	10797	10022	10492	10752	9992	10468	10744
1.00	61.113	17384	18147	18499	16770	17407	17739	16897	17568	17903	16844	17500	17833	16789	17470	17827
1.10	56.072	24974	25995	26411	24122	24997	25385	24310	25228	25621	24240	25135	25525	24155	25088	25514
1.20	53.429	32808	34103	34568	31700	32836	33268	31969	33158	33597	31887	33039	33471	31771	32963	33438
1.30	48.314	39726	41129	41615	38513	39783	40238	38830	40155	40618	38760	40031	40483	38617	39923	40416
1.50	38.432	49953	51355	51853	48998	50382	50864	49259	50675	51163	49231	50586	51060	49051	50433	50943
1.75	29.171	55899	57130	57642	55485	56838	57358	55596	56941	57462	55595	56915	57430	55444	56787	57331
2.00	22.855	57688	58693	59243	57335	58525	59102	57444	58609	59180	57456	58615	59186	57299	58503	59083
4.00	10.589	59495	60316	60926	58738	59825	60483	59006	60031	60672	59037	60063	60704	58768	59872	60543

Y	α	CCSD(TQ),b			CR-CCSD(TQ),a			CR-CCSD(TQ),b			CR-CC(2,3)+Q(a)[b]			CR-CC(2,3)+Q(b)[b]		
		$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$
0.80	78.808	4535	4838	5008	4549	4858	5029	4551	4861	5032	4510	4821	4999	4513	4824	5002
0.90	69.118	9945	10416	10676	9969	10452	10715	9973	10458	10721	9905	10385	10662	9909	10390	10668
1.00	61.113	16727	17385	17717	16767	17443	17779	16772	17450	17787	16659	17345	17703	16664	17352	17711
1.10	56.072	24067	24966	25357	24138	25061	25457	24140	25067	25464	23983	24921	25349	23986	24926	25356
1.20	53.429	31631	32797	33234	31765	32958	33400	31759	32957	33401	31568	32764	33242	31562	32763	33242
1.30	48.314	38454	39757	40218	38655	39979	40444	38633	39964	40430	38442	39747	40242	38420	39732	40229
1.50	38.432	48996	50402	50891	49211	50615	51101	49177	50584	51072	49003	50372	50881	48970	50341	50851
1.75	29.171	55500	56837	57361	55636	56968	57487	55605	56937	57457	55484	56814	57356	55452	56783	57326
2.00	22.855	57312	58468	59047	57498	58653	59225	57463	58618	59191	57354	58548	59128	57318	58512	59094
4.00	10.589	58689	59724	60384	59036	60058	60701	59014	60025	60670	58798	59899	60572	58776	59866	60541

The approximate minimum energy path, determined using the potential function of Ref. [102], is defined by the coordinate Y (in Å), which is the distance between O and the line connecting both H nuclei, and the H–O–H angle α (in degree). The equilibrium values of Y and α are $Y_e = 0.58641$ Å and $\alpha_e = 104.501$ degree [109]. All energies E (in cm^{-1}) are reported as $E - E(Y_e, \alpha_e)$, where $E(Y_e, \alpha_e)$ are the corresponding values of E at the equilibrium geometry. X is a cardinal number defining the aug-cc-pCVXZ basis sets used in the calculations. In all CC calculations, all electrons were correlated

[a] Equivalent to the CCSD(2)$_T$ approach of Ref. [38]

[b] CR-CC(2, 3)+Q(x) = CR-CC(2, 3) + [CR-CCSD(TQ), x − CR-CCSD(T)], x = a, b

approach is also erratic in the case of cut (iii), in which two O–H bonds have to be significantly stretched during the formation of the $H_2(X\ ^1\Sigma_g^+)$ and $O(2p^4\ ^1D)$ products, although the errors relative to MRCI(Q) are not as large in this case as in the other two cuts. One of the reasons is that unlike cuts (i) and (ii), which lead to the fragmentations of the closed-shell water molecule on the singlet ground-state surface into open-shell (doublet or even triplet) products, which introduce very large non-dynamic correlation effects, the minimum energy path that defines cut (iii) leads to the formation of the closed-shell ($H_2(X\ ^1\Sigma_g^+)$) or singlet ($O(2p^4\ ^1D)$) fragments while the O–H bonds are broken. Moreover, the hydrogen product molecule is a two-electron system, which is described exactly by the CCSD approach. These differences between cuts (i) and (ii), on the one hand, and cut (iii), on the other hand, can be seen by examining the largest doubly excited (T_2) cluster amplitudes. The largest spin-free T_2 amplitude, which corresponds to the HOMO → LUMO double excitation at $R = 5R_e$ of cut (i) equals, according to the CCSD/$X = 4$ calculations, −0.858278 (this is a single-bond breaking case, so other T_2 amplitudes are much smaller). The two largest T_2 amplitudes, which correspond to the HOMO → LUMO and (HOMO − 1) → (LUMO + 1) double excitations at $R = 5R_e$ of cut (ii) equal, according to the CCSD/$X = 4$ calculations, −0.774880 and −0.774382, respectively (clearly, there are a few other large T_2 amplitudes in this case, which engage the highest two occupied and lowest two unoccupied orbitals, since this is a double dissociation of water into $2H(1s\ ^2S) + O(2p^4\ ^3P)$ that involves, in the zero-order description, four active orbitals and four electrons). For comparison, the largest T_2 amplitudes along the minimum energy path defining cut (iii) never exceed

Table 6 The differences between CC/CR-CC energies, calculated relative to their equilibrium values (the CC/CR-CC $[E - E(R_e, \alpha_e)]$ values in Table 3) and the corresponding MRCI(Q) relative energies (the MRCI(Q) $[E - E(R_e, \alpha_e)]$ values in Table 2) for the dissociation of a single O–H bond in water (into $H(1s\ ^2S) + OH(X\ ^2\Pi)$; cut (i))

R	CCSD			CCSD(T)			CR-CCSD(T)			CR-CC(2,3),A[a]			CR-CC(2,3)		
	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$
$1.25R_e$	280	306	308	43	4	−3	92	70	65	72	42	35	57	39	39
$1.50R_e$	642	695	701	78	11	−2	206	176	167	160	110	97	118	96	97
$1.75R_e$	1132	1253	1270	89	19	6	365	363	356	286	243	227	175	186	186
$2.00R_e$	1822	2077	2124	42	5	5	608	687	698	487	490	483	248	321	351
$2.50R_e$	3421	4031	4168	−667	−649	−619	1115	1410	1469	889	1019	1039	369	662	725
$3.00R_e$	4479	5347	5554	−2134	−2211	−2195	1307	1726	1811	997	1185	1213	326	706	813
$4.00R_e$	5207	6277	6539	−4385	−4732	−4785	1250	1726	1818	871	1068	1092	168	584	720
$5.00R_e$	5355	6479	6754	−5211	−5689	−5779	1137	1611	1699	746	934	954	93	490	625
R	CCSD(TQ),b			CR-CCSD(TQ),a			CR-CCSD(TQ),b			CR-CC(2,3)+Q(a)[b]			CR-CC(2,3)+Q(b)[b]		
	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$
$1.25R_e$	18	−10	−16	40	20	16	41	22	18	5	−11	−10	6	−9	−8
$1.50R_e$	20	−30	−41	91	64	56	90	65	58	2	−16	−14	1	−15	−12
$1.75R_e$	−17	−64	−74	178	179	174	170	175	172	−12	2	5	−21	−1	2
$2.00R_e$	−119	−128	−124	353	433	445	331	417	432	−7	67	99	−30	51	86
$2.50R_e$	−885	−845	−811	781	1063	1122	729	1020	1084	36	315	378	−16	272	339
$3.00R_e$	−2287	−2366	−2354	961	1351	1433	911	1308	1394	−20	330	434	−70	287	395
$4.00R_e$	−4308	−4714	−4782	904	1330	1417	907	1341	1431	−179	188	319	−175	199	333
$5.00R_e$	−5006	−5568	−5679	765	1179	1262	828	1255	1341	−280	58	187	−216	135	267

X is a cardinal number defining the aug-cc-pCVXZ basis sets used in the calculations

[a] Equivalent to the CCSD(2)$_T$ approach of Ref. [38]

[b] CR-CC(2, 3)+Q(x) = CR-CC(2, 3) + [CR-CCSD(TQ), x − CR-CCSD(T)], x = a, b

≈ 0.2 and are usually considerably smaller. This explains the observed differences in the performance of the CCSD and various CCSD-based non-iterative CC methods in the calculations for cut (iii), where the overall behavior of the single-reference CC methods, although not perfect, remains quite reasonable, and the other two cuts examined in this work, where the standard CC approximations, including CCSD, CCSD(T), and CCSD(TQ),b, display dramatic failures.

The above discussion confirms the known fact that one has to go beyond the basic CCSD approximation and account for higher-than-doubly excited clusters to obtain a quantitatively accurate description of the potential energy surface, even in the vicinity of the equilibrium geometry. This is often done with the CCSD(T) approach, which describes the leading effects due to triply excited clusters via non-iterative corrections to the CCSD energy. As shown in our tables, the CCSD(T) approach provides excellent results that almost perfectly agree with the results of MRCI(Q) calculations, when stretches of the O–H bonds are small. For example, in the case of cut (i), the differences between the CCSD(T)/X = 4 and MRCI(Q)/X = 4 energies do not exceed 6 cm^{-1} up to $R = 2R_e$ and for cut (ii) they remain smaller than 38 cm^{-1} up to $R = 1.5R_e$. This is impressive, if we realize that the $R \approx 2R_e$ and $R \approx 1.5R_e$ regions of cuts (i) and (ii), respectively, are characterized by the energies of ≈ 36, 000 cm^{-1}. A similarly impressive performance of CCSD(T) is observed for other aug-cc-pCVXZ basis sets, although we should note a rather substantial error increase, relative to MRCI(Q), when the $X = 2$ basis sets is employed (particularly for cuts (i) and (ii); cf. Tables 6 and 7). Interestingly enough, in the case of cut (ii), the CCSD(T) results remain reasonable up to ∼67,000 cm^{-1} or $R \approx 2R_e$ (unsigned errors relative to MRCI(Q) on the order of 200–300 cm^{-1}). One has to be very careful, however, in interpreting these high accuracies obtained with CCSD(T) for small and, in the case of cut (ii), intermediate stretches of the O–H bonds, particularly that CCSD(T) eventually suffers significant breakdowns and it may not always be easy to predict when one should stop trusting the CCSD(T) approach. Indeed, if we correct the CCSD(T) results for the dominant effects due to quadruply excited clusters, as is done by the CCSD(TQ),b approach, which can only improve the quality of CC calculations in non-degenerate regions of the potential energy surface, the agreement between the CC

Table 7 The differences between CC/CR-CC energies, calculated relative to their equilibrium values (the CC/CR-CC $[E - E(R_e, \alpha_e)]$ values in Table 4) and the corresponding MRCI(Q) relative energies (the MRCI(Q) $[E - E(R_e, \alpha_e)]$ values in Table 2) for the C_{2v}-symmetric double dissociation of water (into $2H(1s\ ^2S) + O(2p^4\ ^3P)$; cut (ii))

R	CCSD			CCSD(T)			CR-CCSD(T)			CR-CC(2,3),A[a]			CR-CC(2,3)		
	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$
$1.25R_e$	600	657	662	93	14	1	206	164	154	160	100	86	107	73	79
$1.50R_e$	1466	1594	1609	189	65	38	530	488	469	402	313	286	274	233	254
$1.75R_e$	2644	2942	2984	197	91	66	1028	1071	1059	741	690	660	474	538	547
$2.00R_e$	4063	4703	4808	−285	−246	−232	1612	1889	1917	949	1061	1059	381	647	709
$2.50R_e$	5156	7068	7460	−7302	−6486	−6258	845	2097	2329	−2012	−1260	−1111	−3314	−2230	−1971
$3.00R_e$	3398	6065	6646	−19659	−19279	−19133	−1862	−170	157	−6334	−5746	−5647	−7760	−6904	−6589
$4.00R_e$	1436	4321	4956	−33244	−34423	−34697	−4293	−2579	−2258	−9433	−9079	−9052	−10497	−9854	−9636
$5.00R_e$	859	3750	4388	−37103	−38961	−39412	−5032	−3360	−3049	−10291	−9999	−9985	−11098	−10542	−10563

R	CCSD(TQ),b			CR-CCSD(TQ),a			CR-CCSD(TQ),b			CR-CC(2,3)+Q(a)[b]			CR-CC(2,3)+Q(b)[b]		
	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$
$1.25R_e$	38	−17	−29	89	52	44	93	58	50	−10	−39	−31	−6	−34	−25
$1.50R_e$	46	−42	−65	243	207	191	246	215	202	−13	−49	−24	−10	−40	−13
$1.75R_e$	−45	−118	−138	548	589	580	533	587	582	−7	56	69	−21	53	71
$2.00R_e$	−334	−363	−366	1073	1307	1329	1061	1296	1323	−158	64	121	−170	53	115
$2.50R_e$	1015	−635	−915	1996	2880	3040	3345	3827	3908	−2164	−1447	−1260	−815	−500	−391
$3.00R_e$	16806	9551	8069	2740	3957	4194	6602	7174	7270	−3158	−2778	−2553	705	439	523
$4.00R_e$	49303	35878	33021	5449	6868	7159	8956	9957	10155	−755	−407	−219	2752	2683	2777
$5.00R_e$	62544	47428	44150	8149	9660	9978	9188	10333	10566	2083	2477	2465	3122	3150	3053

X is a cardinal number defining the aug-cc-pCVXZ basis sets used in the calculations

[a] Equivalent to the CCSD(2)$_T$ approach of Ref. [38]

[b] CR-CC(2, 3)+Q(x) = CR-CC(2, 3) + [CR-CCSD(TQ), x − CR-CCSD(T)], x = a, b

and MRCI(Q) results in the $R \leq 2R_e$ regions of cuts (i) and (ii) is no longer as impressive as in the CCSD(T) case. For example, the −2 and 5 cm^{-1} differences between the CCSD(T)/$X = 4$ and MRCI(Q)/$X = 4$ energies obtained for cut (i) at $R = 1.5R_e$ and $2R_e$ increase to −41 and −124 cm^{-1}, respectively, when the CCSD(TQ),b method is employed. The 1 and 38 cm^{-1} differences between the CCSD(T)/$X = 4$ and MRCI(Q)/$X = 4$ energies obtained for cut (ii) at $R = 1.25R_e$ and $1.5R_e$ increase, in absolute value, to 29 and 65 cm^{-1}, when instead of CCSD(T) we use the CCSD(TQ),b method. This means that either the CCSD(T) results are very accurate due to fortuitous cancellation of errors or the MRCI(Q) results that we use as a benchmark are not as accurate as the CCSD(TQ),b results in the region of smaller stretches of the O–H bonds, where CCSD(TQ),b can be safely applied, creating a false impression about superb accuracy of the CCSD(T) approximation. Clearly, both interpretations are possible. For example, the CCSD(T) approach is known to provide the results which are often better than those obtained with the full CCSDT method, which makes no physical sense whatsoever. We believe that in the case of water the CCSD(TQ),b approach is more accurate than MRCI(Q) in the spectroscopic region and moderate stretches of the O–H bond(s), although both methods provide high quality results. Our belief is based on the fact that the CCSD(TQ),b method includes higher-order dynamical correlation effects, which dominate in the spectroscopic region and which are not present in MRCI(Q). The overall superiority of CCSD(TQ),b over MRCI(Q) for moderate stretches of the O–H bond(s) can be seen by comparing the differences between the CCSD(TQ),b/$X = 4$ and ES energies in the $R \leq 2R_e$ regions of cuts (i) and (ii) with the corresponding differences between the MRCI(Q)/$X = 4$ and ES energies. This illustrates the well-known advantage of using the CC methods over MRCI techniques, which are not as effective in accounting for the dynamical correlation effects that dominate electron correlations near the equilibrium geometry as the high-level CC approaches. Interestingly enough, further increase of the basis set makes the agreement between the MRCI(Q) and ES surfaces in the region of smaller stretches of the O–H bond(s), where the ES potential function is nearly spectroscopic, even worse (cf. the MRCI(Q)/$X =$ 4 and MRCI(Q)/$X = 5$ results in Table 9). The superiority of the CCSD(TQ),b and related CCSD(TQ$_f$) methods,

Table 8 The differences between CC/CR-CC energies, calculated relative to their equilibrium values (the CC/CR-CC $[E - E(R_e, \alpha_e)]$ values in Table 5) and the corresponding MRCI(Q) relative energies (the MRCI(Q) $[E - E(R_e, \alpha_e)]$ values in Table 2) for the C_{2v} dissociation of water into $H_2(X\ ^1\Sigma_g^+)$ and $O(2p^4\ ^1D)$ along the approximate minimum energy path determined using the potential function of Ref. [102] (cut (iii))

Y	α	CCSD			CCSD(T)			CR-CCSD(T)			CR-CC(2,3),A[a]			CR-CC(2,3)		
		$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$
0.80	78.808	273	317	322	54	38	36	96	95	93	78	71	68	57	58	63
0.90	69.118	488	554	562	89	58	52	168	162	158	134	118	113	104	94	105
1.00	61.113	742	821	833	128	81	73	255	242	237	202	174	167	147	144	161
1.10	56.072	1021	1108	1124	169	110	98	357	341	334	287	248	238	202	201	227
1.20	53.429	1311	1404	1420	203	137	120	472	459	449	390	340	323	274	264	290
1.30	48.314	1425	1506	1520	212	160	143	529	532	523	459	408	388	316	300	321
1.50	38.432	1159	1184	1191	204	211	202	465	504	501	437	415	398	257	262	281
1.75	29.171	557	526	526	143	234	242	254	337	346	253	311	314	102	183	215
2.00	22.855	918	1030	1062	565	862	921	674	946	999	686	952	1005	529	840	902
4.00	10.589	1961	2258	2336	1204	1767	1893	1472	1973	2082	1503	2005	2114	1234	1814	1953
Y	α	CCSD(TQ),b			CR-CCSD(TQ),a			CR-CCSD(TQ),b			CR-CC(2,3)+Q(a)[b]			CR-CC(2,3)+Q(b)[b]		
		$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$	$X=2$	$X=3$	$X=4$
0.80	78.808	34	29	27	48	49	48	50	52	51	9	12	18	12	15	21
0.90	69.118	57	42	37	81	78	76	85	84	82	17	11	23	21	16	29
1.00	61.113	85	59	51	125	117	113	130	124	121	17	19	37	22	26	45
1.10	56.072	114	79	70	185	174	170	187	180	177	30	34	62	33	39	69
1.20	53.429	134	98	86	268	259	252	262	258	253	71	65	94	65	64	94
1.30	48.314	153	134	123	354	356	349	332	341	335	141	124	147	119	109	134
1.50	38.432	202	231	229	417	444	439	383	413	410	209	201	219	176	170	189
1.75	29.171	158	233	245	294	364	371	263	333	341	142	210	240	110	179	210
2.00	22.855	542	805	866	728	990	1044	693	955	1010	584	885	947	548	849	913
4.00	10.589	1155	1666	1794	1502	2000	2111	1480	1967	2080	1264	1841	1982	1242	1808	1951

X is a cardinal number defining the aug-cc-pCVXZ basis sets used in the calculations

[a] Equivalent to the CCSD(2)$_T$ approach of Ref. [38]

[b] CR-CC(2, 3)+Q(x) = CR-CC(2, 3) + [CR-CCSD(TQ), x − CR-CCSD(T)], x = a, b

which account for triply and quadruply excited clusters, over CCSD(T), which ignores the latter clusters, in applications involving potential energy surfaces near the equilibrium geometry is well-documented as well (cf., e.g., Refs. [11–13, 19,20,30,32,57,127–129]) and our calculations confirm this superiority, in spite of the tiny (and misleading) differences between the CCSD(T) and MRCI(Q) energies for cuts (i) and (ii).

Before discussing the failures of the CCSD(T) and CCSD(TQ),b methods at larger O–H separations of cuts (i) and (ii) and improvements offered by the CR-CC methods, which are quite apparent when we examine the results shown in Tables 3 to 8, let us point out that in the case of cut (iii), the behavior of the CCSD(T) and CCSD(TQ),b methods vs. the MRCI(Q) approach is somewhat different, when compared to the other two cuts explored in this work. As already pointed out above, the doubly excited (also, singly excited) cluster amplitudes along the minimum energy path defining cut (iii) never become large and the corresponding $H_2(X\ ^1\Sigma_g^+)$ and $O(2p^4\ ^1D)$ dissociation products are of the closed-shell ($H_2(X\ ^1\Sigma_g^+)$) or open-shell singlet ($O(2p^4\ ^1D)$) type. Thus, it is not completely surprising to observe the relatively good performance of the standard single-reference CCSD(T) and CCSD(TQ),b approaches in the entire region of Y values shown in our tables (with the exception, perhaps, of the last two points, $Y = 2.0$ and 4.0 Å, although we must remember that these points are located at more than 58,000 cm^{-1} above the global minimum, which makes the ∼500–1,900 cm^{-1} errors relatively small, particularly for the relatively inexpensive single-reference calculations using the RHF reference; cf. the discussion below for the additional remarks). In particular, the differences between the CCSD(T) and MRCI(Q) energies do not exceed 250 cm^{-1} in the entire $Y_e \leq Y \leq 1.75$ Å region, in which energies become as large as

Table 9 The differences between the CR-CC(2,3)+Q(b) and MRCI(Q) energies obtained with the aug-cc-pCVQZ ($X = 4$) basis, the differences between the CR-CC(2,3)+Q(b)/aug-cc-pCVQZ and ES energies, and the differences between the MRCI(Q)/aug-cc-pCVXZ ($X = 4, 5$) and ES energies (all energies calculated relative to their corresponding equilibrium values, as in the earlier tables) for the three cuts of the water potential energy surface: (i) the dissociation of a single O–H bond, (ii) the C_{2v}-symmetric dissociation of both O–H bonds, and (iii) the C_{2v} dissociation into $H_2(X\ ^1\Sigma_g^+)$ and $O(2p^4\ ^1D)$ (see Table 2 for the definitions of R and Y, the corresponding values of the H–O–H angle α, and the equilibrium values of R, Y, and α). All energy differences are in cm^{-1}

R	CR-CC(2,3)+Q(b)/X=4 −MRCI(Q)/X=4	CR-CC(2,3)+Q(b)/X=4 −ES	MRCI(Q)/X=4 −ES	MRCI(Q)/X=5 −ES
$H_2O(\tilde{X}\ ^1A_1) \rightarrow H(1s\ ^2S) + OH(X\ ^2\Pi)$				
$1.25R_e$	−8	−21	−13	29
$1.50R_e$	−12	116	128	197
$1.75R_e$	2	−17	−19	71
$2.00R_e$	86	118	32	138
$2.50R_e$	339	1051	712	833
$3.00R_e$	395	861	466	591
$4.00R_e$	333	277	−56	69
$5.00R_e$	267	134	−133	−8
$H_2O(\tilde{X}\ ^1A_1) \rightarrow 2H(1s\ ^2S) + O(2p^4\ ^3P)$				
$1.25R_e$	−25	−11	14	98
$1.50R_e$	−13	541	554	691
$1.75R_e$	71	666	595	778
$2.00R_e$	115	491	376	596
$2.50R_e$	−391	−448	−57	204
$3.00R_e$	523	145	−378	−107
$4.00R_e$	2777	2338	−439	−171
$5.00R_e$	3053	2629	−424	−157
Y	CR-CC(2,3)+Q(b)/X=4 −MRCI(Q)/X=4	CR-CC(2,3)+Q(b)/X=4 −ES	MRCI(Q)/X=4 −ES	MRCI(Q)/X=5 −ES
$H_2O(\tilde{X}\ ^1A_1) \rightarrow H_2(X\ ^1\Sigma_g^+) + O(2p^4\ ^1D)$				
0.80	21	4	−17	25
0.90	29	8	−21	41
1.00	45	−216	−261	−182
1.10	69	−1233	−1302	−1206
1.20	94	−3084	−3178	−3066
1.30	134	−3497	−3631	−3511
1.50	189	−1286	−1475	−1351
1.75	210	15	−195	−75
2.00	913	608	−305	−192
4.00	1951	1845	−106	−2

$\sim$57,000 cm^{-1} (recall that $Y_e = 0.58641$ Å), and are smaller than 100 cm^{-1} when Y does not exceed 1.1 Å (energies below $\sim$27,000 cm^{-1}). The CCSD(TQ),b approach reduces these differences even further, showing a nice and systematic behavior of the single-reference CC theory in this case. Clearly, it is interesting to examine if the CR-CC approaches, which are primarily designed to improve the CC results when a system is fragmented into open-shell fragments, can maintain the high accuracies of the CCSD(T) and CCSD(TQ),b calculations and systematic improvements in the results when going from the triples to the quadruples levels of CC theory in the case of the minimum energy path that leads to the singlet, but non-closed-shell products.

One issue that we do not address in this study and that may affect the results of all CC and CR-CC calculations in the $Y \geq 2.0$ Å region of cut (iii) (and, perhaps, the best CR-CC results in the $R > 3R_e$ region of cut (ii)) is the issue of the existence of the avoided crossings of ground and excited states

of water at larger internuclear separations (see, e.g., Refs. [113,114,118,119] and references therein). For example, it is possible that for the larger, but not the largest, values of Y of cut (ii), where the H–H bond is still somewhat stretched, other dissociation channels, such as $H_2(b\ ^3\Sigma_u^+) + O(2p^4\ ^3P)$, compete with the ground-state $H_2(X\ ^1\Sigma_g^+) + O(2p^4\ ^1D)$ channel and that the CCSD solutions that we found, for example, at $Y = 4.0$ Å, are not necessarily the solutions that correlate with the lowest-energy state of water of the $^1A_1$ symmetry. This would explain a steep increase in the errors of the CCSD(T), CCSD(TQ),b, and all, otherwise very accurate, CR-CC calculations in the $Y \geq 2.0$ Å region of cut (iii), from ∼200–400 cm^{-1} at $Y = 1.75$ Å to ∼1,800–2,100 cm^{-1} at $Y = 4.0$ Å. We tried to find other CCSD solutions in the $Y \geq 2.0$ Å region, but we have not been successful. Thus, it may be necessary to calculate other electronic states in the $Y \geq 2.0$ Å region, which one can try to do using, for example, the excited-states CR-CC methods, such as CR-EOMCCSD(T) [87,88], and the excited-state variant of CR-CC(2,3) tested in Refs. [14,44], in which the properly renormalized triples corrections are added to the energies obtained in the equation-of-motion (EOM) CCSD calculations. It is not unusual to observe the switching between the ground and low-lying excited states of the same symmetry in CC/EOMCC calculations in the vicinity of avoided crossings [130]. The state-switching of this type would explain the larger errors in the $Y \geq 2.0$ Å region observed in our CC calculations. We will examine this issue in the future.

Much of the above discussion points to the importance of properly balancing various correlation effects and the need to account for the triple as well as quadruple excitations in the high quality calculations of molecular potential energy surfaces. The properly constructed theory should provide an accurate description of triply, quadruply, and, if need be, other higher-order clusters, without the fortuitous cancellation of errors that the CCSD(T) approach displays. Clearly, the good theory should also eliminate the significant failures of the CCSD(T), CCSD(TQ),b, and other similar methods at larger internuclear separations or at least be more robust in this regard. In the case of the water potential examined in this work, these failures are dramatic. As shown in Tables 3 to 8 (particularly, Tables 6 to 8), the unsigned errors in the CCSD(T)/$X = 2 - 4$ energies, relative to the corresponding MRCI(Q)/$X = 2 - 4$ data, range between 619 and 5,779 cm^{-1}, when the $R = 2.5R_e - 5R_e$ region of cut (i) is examined, and 6,258 and 39,412 cm^{-1}, when the $R = 2.5R_e - 5R_e$ region of cut (ii) is explored, and the CCSD(T) energies go considerably below the MRCI(Q) energies. The CCSD(TQ),b approach does not improve the situation at all, producing the 811–5,679 cm^{-1} unsigned errors, relative to MRCI(Q), in the $R = 2.5R_e - 5R_e$ region of cut (i) and the 635–62,544 cm^{-1} unsigned errors, relative to the corresponding MRCI(Q) data, in the $R = 2.5R_e - 5R_e$ region of cut (ii). Unlike CCSD(T), the CCSD(TQ),b energies are significantly above the corresponding MRCI(Q) energies at larger O–H separations of cut (ii), while being below the MRCI(Q) energies for cut (i). All of this demonstrates the divergent behavior of the standard single-reference CC methods, caused by the large non-dynamic correlation effects (which manifest themselves through large doubly excited cluster amplitudes, as described above), the poor description of the wave function by the CCSD approach, on which the CCSD(T) and CCSD(TQ),b methods rely, and the strongly divergent nature of the many-body perturbation theory (MBPT) series, on which the standard (T) and (TQ) energy corrections are based, in the regions of larger internuclear separations.

As shown in Tables 6 to 8, the CR-CCSD(T) method provides considerable improvements in the CCSD(T) results for the single-bond breaking defining cut (i), reducing, for example, the 4,385–4,785 cm^{-1} and 5,211–5,779 cm^{-1} errors in the CCSD(T)/$X = 2 - 4$ energies at $R = 4R_e$ and $5R_e$, relative to the corresponding MRCI(Q)/$X = 2 - 4$ data, to 1,250–1,818 cm^{-1} and 1,137–1,699 cm^{-1}, respectively. The CR-CCSD(TQ),a and CR-CCSD(TQ),b methods provide further improvements and a nice and smooth description of the entire cut (i), with an exception, perhaps, of the last point at $R = 5R_e$, where a small error reduction compared to $R = 4R_e$ may be a signature of the eventual problems somewhere in the $R \gg 5R_e$ region, although we are not sure about it at this time. For example, the differences between the CR-CCSD(TQ),b/$X = 4$ and MRCI(Q)/$X = 4$ energies smoothly increase with R, from 18 and 58 cm^{-1} at $R = 1.25R_e$ and $1.5R_e$, respectively (energies on the order of 7,400 and 18,900 cm^{-1}), to 432 cm^{-1} at $R = 2R_e$, and 1,431 cm^{-1} at $R = 4R_e$, where the energy is almost 44,000 cm^{-1}. The situation for the more challenging cut (ii), where both O–H bonds are broken, is, at least to some extent, similar to that observed in the case of cut (i), with the CR-CCSD(TQ),a and CR-CCSD(TQ),b methods eliminating the pathological behavior of CCSD(T) and CCSD(TQ),b at larger stretches of both O–H bonds. Again, we observe a smooth increase of the differences between the CR-CCSD(TQ),a or CR-CCSD(TQ),b and MRCI(Q) energies with R, from 44 (50) and 191 (202) cm^{-1} at $R = 1.25R_e$ and $1.5R_e$, where energies are on the order of ∼14,000 and 36,000 cm^{-1}, respectively, through 1,329 (1,323) cm^{-1} at $R = 2R_e$, where the energy exceeds 67,000 cm^{-1}, and 9,978 (10,566) cm^{-1} at $R = 5R_e$, where the energies exceed 81,000 cm^{-1}, when the CR-CCSD(TQ),a/$X = 4$ (CR-CCSD(TQ),b/$X = 4$) results are examined. We do not claim that these are superb results, but it is quite encouraging to see that the CR-CC methodology is capable of providing significant improvements over the standard CC results, even when the double dissociation of water is examined. There is, of course, a difference between the behavior of the CR-CCSD(T) method in the case of the double O–H dissociation defining cut (ii) and the

single-bond breaking defining cut (i). The CR-CCSD(T) approach provides a reasonably smooth description of cut (i), while failing in the case of cut (ii). This is a consequence of ignoring the quadruply excited clusters in the CR-CCSD(T) calculations, which are absolutely critical in cases of double bond breaking (while improving accuracies in the calculations for single-bond breaking). It is interesting to observe, though, the substantial improvements in the poor CCSD(T) results in the $R = 2.5R_e - 5R_e$ region of cut (ii) by the CR-CCSD(T) approach (error reduction in the $X = 4$ calculations at $R = 5R_e$, relative to the corresponding MRCI(Q)/$X = 4$ result, from more than 39,000 cm^{-1} in the CCSD(T) case to $\approx$ 3,000 cm^{-1} in the CR-CCSD(T) case). It is also interesting to observe that the CR-CCSD(T), CR-CCSD(TQ),a, and CR-CCSD(TQ),b approaches provide a relatively accurate and smooth description of the "easier" cut (iii) as well. In this case, as pointed out above, the conventional CCSD(T) and CCSD(TQ),b approximations work quite well, but it is good to see that the CR-CCSD(T) and CR-CCSD(TQ),x (x = a, b) methods are, more or less, equally effective, with the CR-CCSD(TQ),x approaches providing systematic improvements over the relatively good CR-CCSD(T) results. The ~90–530 cm^{-1} differences between the CR-CCSD(T) and MRCI(Q) energies and the slightly smaller ~50–440 cm^{-1} differences between the CR-CCSD(TQ),x and MRCI(Q) energies in the entire $Y = 0.8 - 1.75$ Å region, where energies grow from about 5,000 to more than 57,000 cm^{-1} above the global minimum, is clearly an encouraging result, confirming the usefulness of the CR-CC methods.

The CR-CCSD(T) and CR-CCSD(TQ),x (x = a, b) methods provide substantial improvements in the regions of larger internuclear separations, where the standard CCSD(T) and CCSD(TQ),b approaches fail, but it would be useful to achieve further error reduction in the CR-CC calculations, particularly in the cases of cuts (i) and (ii), which are more challenging for the single-reference CC methods than cut (iii). It would also be useful to improve the results of CR-CC calculations in the vicinity of the equilibrium region, where the CCSD(T) and CCSD(TQ),b methods are somewhat more accurate than the CR-CCSD(T) and CR-CCSD(TQ),x (x = a, b) approaches. As explained in Refs. [41,42], the recently proposed CR-CC(2,3) theory not only eliminates the small size extensivity errors from the CR-CCSD(T) results (which in the case of water are negligible, since water molecule is a small, 10-electron system), but it also improves the accuracy of CR-CCSD(T) calculations by adding various product terms involving the singly and doubly excited clusters and the triply excited moments of the CCSD equations to the bare triexcited moment terms that are already present in the CR-CCSD(T) triples correction formula [131]. It is, therefore, interesting to examine the performance of the CR-CC(2,3) approach using the three cuts of the water potential examined in this work. Since we have already noticed the importance of quadruply excited clusters in improving the results, particularly for the double O–H dissociation defining cut (ii), it is also useful to investigate if correcting the CR-CC(2,3) results for quadruples through the CR-CC(2,3)+Q(a) and CR-CC(2,3)+Q(b) methods described in the Introduction gives the desired high accuracies for a wide range of nuclear geometries of the water system explored in this work. Following the discussion of the CR-CC(2,3) theory in Refs. [41,42,44], we consider two variants of CR-CC(2,3) in this study, namely, the complete variant D, for which we continue to use an acronym CR-CC(2,3) without additional letters, and the approximate variant A, called CR-CC(2,3),A, which is obtained by replacing the diagonal matrix elements of the similarity-transformed Hamiltonian of CCSD involving triply excited determinants, which enter the triples correction of CR-CC(2,3), by the usual MBPT denominator defining triple excitations, i.e., $(\epsilon_a + \epsilon_b + \epsilon_c - \epsilon_i - \epsilon_j - \epsilon_k)$. The CR-CC(2,3),A approach is equivalent to the CCSD(2)$_T$ method of Ref. [38].

As shown in Tables 3 to 8, the CR-CC(2,3),A (= CCSD(2)$_T$) and full CR-CC(2,3) (= CR-CC(2, 3), D) approaches provide improvements in the CR-CCSD(T) results for the single-bond breaking defining cut (i) and the C_{2v} dissociation pathway into $H_2(X\ ^1\Sigma_g^+)$ and $O(2p^4\ ^1D)$ in the entire regions of the corresponding R and Y values. They also improve the description of the double dissociation of water defining cut (ii) by the CR-CCSD(T) method in the $R = R_e - 2.5R_e$ region. For example, in the case of cut (i), the CR-CC(2,3),A approach reduces the 65, 167, 698, 1,811, and 1,699 cm^{-1} errors in the CR-CCSD(T)/$X = 4$ results, relative to the corresponding MRCI(Q)/$X = 4$ data, at $R = 1.25R_e$, $1.5R_e$, $2R_e$, $3R_e$, and $5R_e$ to 35, 97, 483, 1,213, and 954 cm^{-1}, respectively. With an exception of $R = 1.25R_e$ and $1.5R_e$, where errors remain almost unchanged, the full CR-CC(2,3) method improves the agreement with the MRCI(Q)/$X = 4$ energies even further, reducing the 483, 1,213, and 954 cm^{-1} errors in the CR-CC(2,3),A energies, relative to MRCI(Q), at $R = 2R_e$, $3R_e$, and $5R_e$ to 351, 813, and 625 cm^{-1}, respectively. We can clearly see the benefits of using the full CR-CC(2,3) approach, as opposed to CR-CC(2,3),A or CCSD(2)$_T$. Similar benefits are observed, when we compare the results of the CR-CC(2,3),A and full CR-CC(2,3) calculations in the $R = R_e - 2R_e$ region of cut (ii) and for the the entire cut (iii). The 86–1,059 cm^{-1} errors, relative to MRCI(Q), in the CR-CC(2,3),A/$X = 4$ results obtained in the $R = R_e - 2R_e$ region of cut (ii), which are obviously smaller than the 154–1,917 cm^{-1} errors obtained with CR-CCSD(T), reduce to 79–709 cm^{-1}, when the full CR-CC(2,3)/$X = 4$ method is employed. The 68–398 cm^{-1} differences between the CR-CC(2,3),A/$X = 4$ and MRCI(Q)/$X = 4$ energies in the $Y = 0.8 - 1.75$ Å region of cut (iii) reduce to 63–321 cm^{-1}, when the full CR-CC(2,3)/

$X = 4$ method is used. The use of other aug-cc-pCVXZ basis sets does not change any of these accuracy patterns in a substantial manner.

We can conclude that the full CR-CC(2,3) approach, with the complete treatment the diagonal matrix elements of the similarity-transformed Hamiltonian of CCSD involving triply excited determinants, provides the overall best results when compared to all other non-iterative triples methods examined in this work. It is true that the CR-CC(2,3) approach fails in the $R > 2R_e$ region of cut (ii) and it is also true that the CR-CC(2,3) energies for smaller stretches of the O–H bond(s) appear to be somewhat less accurate than the corresponding CCSD(T) energies. We must remember, however, that one needs quadruply excited clusters in the $R > 2R_e$ region of cut (ii), while the perfect agreement between the CCSD(T) and MRCI(Q) data at smaller stretches of the O–H bond(s) is not necessarily a desired behavior. Indeed, the explicit inclusion of quadruples in CC calculations, which can be done in the region of smaller stretches of the O–H bond(s) via the CCSD(TQ),b approach, makes the agreement between the CC and MRCI(Q) data less perfect, as already explained above. These observations agree with the performance of the CR-CC(2,3) approach in a variety of benchmark calculations reported in Refs. [41,42,44], where it has been noted that the CR-CC(2,3) energies are very close to the full CCSDT energies, not only when CCSDT works, but also when it fails, as is the case of multiple bond dissociations. In particular, as shown in Refs. [41,44], the full CCSDT approach completely fails in the $R > 2R_e$ region of the double dissociation of water, analogous to our cut (ii). Thus, the failure of CR-CC(2,3) in the same region is a desired result, since one cannot break both O–H bonds in the water molecule without quadruply excited clusters, and the approximate triples methods, such as CR-CC(2,3), should not be better in this regard than full CCSDT.

In view of the above discussion, it is very important to examine what happens with the CR-CC(2,3) energies if we augment them by quadruples, as is done in the CR-CC(2,3)+Q(a) and CR-CC(2,3)+Q(b) calculations. As shown in Tables 3 to 9, the overall agreement between the CR-CC(2,3)+Q(x) ($x = a, b$) and MRCI(Q) data is quite remarkable. For example, in the case of cut (i), corresponding to the dissociation of a single O–H bond, the 39–351 cm^{-1} unsigned differences between the CR-CC(2,3)/$X = 4$ and MRCI(Q)/$X = 4$ energies in the $R = R_e - 2R_e$ region, in which these energies increase to more than 35,000 cm^{-1}, reduce to 2–86 cm^{-1} when the CR-CC(2,3)+Q(b)/$X = 4$ approach is employed. The CR-CC(2,3)+Q(a)/$X = 4$ method provides similar results, although the somewhat more complete (cf. Table 1) CR-CC(2,3)+Q(b) approximation seems better. The maximum error, relative to MRCI(Q), characterizing the CR-CC(2,3)/$X = 4$ calculations in the entire range of R values, of 813 cm^{-1}, reduces in the CR-CC(2,3)+Q(b)/$X = 4$ calculations to 395 cm^{-1}. Again, the CR-CC(2,3)+Q(a)/$X = 4$ approach is almost as effective. The use of other aug-cc-pCVXZ basis sets leads to similar error reductions.

The 79–709 cm^{-1} differences between the CR-CC(2,3)/$X = 4$ and MRCI(Q)/$X = 4$ energies in the $R = R_e - 2R_e$ region of cut (ii), where both O–H bonds are simultaneously stretched and where the energy goes up to more than 67,000 cm^{-1}, reduce (in absolute value) to 24–121 cm^{-1}, when the CR-CC(2,3)+Q(a)/$X = 4$ method is employed, and 13–115 cm^{-1}, when the CR-CC(2,3)+Q(b)/$X = 4$ approach is used. The CR-CC(2,3)+Q(b) approach remains quite accurate up to $R = 3R_e$, where the energy is already larger than 80,000 cm^{-1}. The difference between the CR-CC(2,3)+Q(b)/$X = 4$ and MRCI(Q)/$X = 4$ energies is only slightly larger than 500 cm^{-1} in the $R = 3R_e$ region. The CR-CC(2,3)+Q(a) approximation shows the signs of unstable behavior in the $R > 2R_e$ region, with the signed errors relative to MRCI(Q) changing from more than +2,000 cm^{-1} to ∼(-3,000)–(-2,000) cm^{-1}, which is partly due to the fact that we use the first-order MBPT estimates of doubly excited cluster amplitudes in defining the (Q) corrections of CR-CC(2,3)+Q(a) (or CR-CCSD(TQ),a [11–13,20]) and partly due to the heuristic nature of the CR-CC(2,3)+Q approaches, which should eventually be replaced by the more consistent CR-CC(2,4) theory. The somewhat ad hoc nature of the CR-CC(2,3)+Q approximations may also be responsible, at least in part, for the ∼ 3,000 cm^{-1} differences between the CR-CC(2,3)+Q(b) and MRCI(Q) energies in the $R = 4R_e - 5R_e$ region of cut (ii). Again, the accuracy patterns observed in the CR-CC(2,3)+Q(a) and CR-CC(2,3)+Q(b) calculations for cut (ii), when compared to MRCI(Q), are essentially independent of the aug-cc-pCVXZ basis set employed in these calculations.

The CR-CC(2,3)+Q(a) and CR-CC(2,3)+Q(b) results for cut (iii), corresponding to the C_{2v} dissociation pathway into $H_2(X\ ^1\Sigma_g^+)$ and $O(2p^4\ ^1D)$, are very good as well. Both CR-CC(2,3)+Q(a) and CR-CC(2,3)+Q(b) methods reduce the errors resulting from the CR-CC(2,3) calculations. The overall accuracy of the CR-CC(2,3)+Q(b) approach in the $Y = 0.8 - 1.75$ Å region of cut (iii), as judged by the differences with MRCI(Q), is better than the accuracy of the CCSD(TQ),b method, which performs very well in this case. It is encouraging to see the relatively small and monotonically increasing 21–210 cm^{-1} differences between the CR-CC(2,3)+Q(b)/$X = 4$ and MRCI(Q)/$X = 4$ energies in the $Y = 0.8 - 1.75$ Å region of cut (iii), where energies go up to ∼ 57,000 cm^{-1} above the minimum.

The overall agreement between the CR-CC(2,3)+Q(b) and MRCI(Q) results for all three potential surface cuts examined in this study is excellent, particularly if we keep in mind the single-reference nature of the CR-CC(2,3)+Q(b) calculations. The fact that with an exception of the $R = 4R_e - 5R_e$ region of cut (ii) and the $Y = 2.0 - 4.0$ Å region of cut (iii), the CR-CC(2,3)+Q(b) and MRCI(Q) energies

agree to within 500 cm^{-1} and, in most cases, to within 100 cm^{-1} or less is a clear demonstration of the large potential offered by the CR-CC theories. The CR-CC(2,3) and CR-CC(2,3)+Q(b) methods seem to be at least as effective as the CCSD(T) and CCSD(TQ),b methods in the vicinity of the equilibrium geometry, where the many-electron correlation effects are primarily of dynamical nature, while providing the accuracy comparable to the MRCI(Q) approach in the higher-energy potential energy surface regions characterized by large non-dynamical correlation effects. In the case of the water molecule, we seem to be able to obtain the relatively small differences between the results of the CR-CC(2,3)+Q(b) and MRCI(Q) calculations, on the order of 100–500 cm^{-1} or less, for the energies as large as 60,000–70,000 cm^{-1} above the global minimum. This is an encouraging finding, considering the single-reference character and the relatively low cost of all CR-CC calculations (cf. Table 1). This is also very promising from the point of view of applying the CR-CC methods in calculations aimed at the construction of accurate global potential functions for dynamical studies. The proximity of the CR-CC(2,3)+Q(b) and MRCI(Q) results for the large portion of the global potential energy surface of water and the fact that the CR-CC(2,3)+Q(b) approach remains as accurate as the CCSD(TQ),b method in the vicinity of the equilibrium geometry open up new avenues for constructing highly accurate global potentials, since switching between the CR-CC(2,3)+Q(b) and MRCI(Q) energies, which are so similar, should be quite straightforward. In the future, we will replace the somewhat heuristic CR-CC(2,3)+Q approximations tested in this work by the properly derived CR-CC(2,4) theory, exploiting the general formalism described in Refs. [41,42]. The excellent CR-CC(2,3)+Q results for water obtained in this work prompt such a development.

Let us, finally, address the issue of the rather substantial differences between the MRCI(Q)/$X = 4$ or MRCI(Q)/$X = 5$ and ES potential energy surfaces in the regions of the intermediate R and Y values, and intermediate or higher, but not the highest energies, which are as much as 700–800 cm^{-1} for cut (i) in the $R \approx 2.5R_e$ region, 600–800 cm^{-1} for cut (ii) in the $R \approx 1.75R_e$ region, and 3,500–3,600 cm^{-1} for cut (iii) in the $Y \approx 1.3$ Å region. Such differences cannot be explained by the neglect of the relativistic, non-adiabatic, and quantum electrodynamical effects in MRCI(Q) calculations. They indicate that either the MRCI(Q) approach employing large basis sets is insufficiently accurate or the ES potential needs further refinement in the above regions. Although both interpretations are possible, we tend to believe that the accuracy of the ES potential function in the regions of intermediate internuclear separations and energies, which connect the spectroscopic and asymptotic regions, is not as high as the accuracy of the ES surface around the minimum, up to about 19,000 cm^{-1}, and in the $H(1s\ ^2S) + OH(X\ ^2\Pi)$, $2H(1s\ ^2S) + O(2p^4\ ^3P)$, and $H_2(X\ ^1\Sigma_g^+) + O(2p^4\ ^1D)$ asymptotic regions. We base our belief on the close proximity of the MRCI(Q) and CR-CC(2,3)+Q(b) energies in the regions of the intermediate R and Y values, where the MRCI(Q)/$X = 4$ or MRCI(Q)/$X = 5$ and ES potentials significantly differ. This is shown in Table 9, where we compare the differences between the best CR-CC(2,3)+Q(b)/$X = 4$ energies and the corresponding MRCI(Q)/$X = 4$ data with the differences between the CR-CC(2,3)+Q(b)/$X = 4$ and ES energies, and the analogous differences between the MRCI(Q)/$X = 4, 5$ and ES energies. As one can see, the 700–800 cm^{-1} differences between the MRCI(Q)/$X = 4, 5$ and ES energies in the $R \approx 2.5R_e$ region of cut (i) are very similar to the $\sim$1,000 cm^{-1} difference between the CR-CC(2,3)+Q(b)/$X = 4$ and ES energies in the same region. The 600–800 cm^{-1} differences between the MRCI(Q)/$X = 4, 5$ and ES energies in the $R \approx 1.75R_e$ region of cut (ii) are not much different than the $\sim$ 700 cm^{-1} difference between the CR-CC(2,3)+Q(b)/$X = 4$ and ES energies in this region. Finally, the 3,500–3,600 cm^{-1} differences between the MRCI(Q)/$X = 4, 5$ and ES energies in the $Y \approx 1.3$ Å region of cut (iii) are very similar to the 3,000–3,500 cm^{-1} differences between the CR-CC(2,3)+Q(b)/$X = 4$ and ES for $Y \approx 1.2 - 1.3$ Å. The large consistency between the MRCI(Q)/$X = 4, 5$ and CR-CC(2,3)+Q(b)/$X = 4$ results in the above regions of the potential energy surface of water makes us believe that the energy values provided by both ab initio approaches in these regions are more accurate than those provided by the existing ES potential. This gives us an opportunity to refine the ES global potential in the future by incorporating some MRCI(Q) or CR-CC(2,3)+Q(b) data from the regions of the intermediate R and Y values in the appropriate fitting and energy switching procedures.

4 Summary and concluding remarks

In this paper, we have explored an issue of the development of single-reference procedures that could be applied to at least some of the most frequent multi-reference situations, such as single and double bond dissociations, by reporting test calculations for the potential energy surface of the water molecule. We have focused on a few basic renormalized CC methods, including the older CR-CCSD(T), CR-CCSD(TQ),a, and CR-CCSD(TQ),b approximations [10–13, 20,29,30], and the most recent size extensive CR-CC(2,3),A (or CCSD(T)$_T$ [38]) and full CR-CC(2,3) approaches that belong to a more general class of CR-CC(m_A, m_B) schemes [41,42,44,131]. In the CR-CCSD(T), CR-CC(2,3),A, and CR-CC(2,3) methods, the relatively inexpensive corrections due to triply excited clusters, similar in the computer cost to the triples corrections of the conventional CCSD(T) theory, are added to the CCSD energy. In the CR-CCSD(TQ),a and CR-CCSD(TQ),b approaches, the CCSD energy is correc-

ted for the dominant effects of triply and quadruply excited clusters in a manner reminiscent of the conventional CCSD(TQ) approximations, such as CCSD(TQ),b [20,32] or CCSD(TQ_f) [19]. Since the CR-CC(2,4) approach has not been fully developed and implemented yet, we have considered two approximate forms of the CR-CC(2,4) theory, abbreviated as CR-CC(2,3)+Q(a) and CR-CC(2,3)+Q(b), in which the CR-CC(2,3) energies are a posteriori corrected for the effect of quadruply excited clusters by using the information about quadruples extracted from the CR-CCSD(TQ),a or CR-CCSD(TQ),b calculations.

In order to examine the performance and benefits of using the single-reference renormalized CC methods, we have compared the results of the CR-CCSD(T), CR-CCSD(TQ),a, CR-CCSD(TQ),b, CR-CC(2,3),A, CR-CC(2,3), CR-CC(2,3) +Q(a), and CR-CC(2,3)+Q(b) calculations for the three important cuts of the potential energy surface of the water molecule, including the dissociation of one O–H bond, which correlates with the $H(1s\ ^2S) + OH(X\ ^2\Pi)$ asymptote, the simultaneous dissociation of both O–H bonds, which leads to the $2H(1s\ ^2S) + O(2p^4\ ^3P)$ products, and the C_{2v}-symmetric dissociation pathway into $H_2(X\ ^1\Sigma_g^+)$ and $O(2p^4\ ^1D)$, with those obtained in the highly accurate MRCI(Q) calculations and those provided by the spectroscopically accurate ES potential function [102]. We have demonstrated that all renormalized CC methods eliminate or considerably reduce the failures of the conventional CCSD(T) and CCSD(TQ),b approaches in the bond breaking regions of the water potential, while retaining high accuracies of the CCSD(T) and CCSD(TQ),b methods in the vicinity of the equilibrium geometry. The full CR-CC(2,3) and CR-CC(2,3)+Q(b) methods are particularly effective in this regard. Unlike CCSD(T), the CR-CC(2,3) approach provides a faithful description of triply excited clusters [41,42,44], even in the equilibrium region, where the CCSD(T) approach works well. After correcting the CR-CC(2,3) results for quadruples, as is done in the CR-CC(2,3)+Q(x) ($x = $ a, b) schemes, we obtain the potential energy surfaces of excellent quality, particularly in the CR-CC(2,3)+Q(b) case. Indeed, as shown in this work, the single-reference, RHF-based, CR-CC(2,3)+Q(b) approach describes the above three cuts of the global potential energy surface of water with accuracies that can only be matched by the high accuracy, CASSCF-based, MRCI(Q) calculations. We find the small differences between the CR-CC(2,3)+Q(b) and MRCI(Q) energies, on the order of 100–500 cm^{-1} or less, for energies as large 60,000–70,000 cm^{-1}, where the highest possible energies corresponding to the complete atomization of water are on the order of 80,000 cm^{-1} and where the existing spectroscopically accurate potentials, such as the ES function, can guarantee very high accuracies up to about 19,000 cm^{-1}, to be the most remarkable finding. At the same time, the CR-CC(2,3)+Q(b) approach, which is based on the excellent description of the triply excited cluster contributions by the size extensive CR-CC(2,3) approximation, corrected for the effects of quadruply excited clusters, provides a balanced description of triples and quadruples in the bond breaking and equilibrium regions. In the equilibrium region, the accuracy of the CR-CC(2,3)+Q(x) ($x = $ a, b) methods is essentially the same as the accuracy of the CCSD(TQ),b approach, which describes the combined effect of triply and quadruply excited clusters in non-degenerate situations extremely well. Thus, the CR-CC(2,3) method corrected for quadruples enables us to bridge the closed-shell and bond breaking regions of the global potential energy surface of water, while preserving the high accuracy of the CCSD(TQ),b results in the closed-shell regions and matching the high quality of MRCI(Q) results in regions of stretched chemical bonds, where CCSD(TQ),b (and CCSD(T), of course) fails.

The excellent agreement between the CR-CC(2,3)+Q(b) and MRCI(Q) results in regions of intermediate stretches of chemical bonds and higher, but not the highest energies, where the ES surface may be somewhat less accurate, has enabled us to suggest ways of improving the global ES potential function of water that might potentially benefit future reaction dynamics and spectroscopic studies. The regions of intermediate stretches of chemical bonds that connect the spectroscopic and asymptotic regions of the water potential energy surface are not as well understood as the spectroscopic and asymptotic regions. Thus, it is difficult to construct the global potential of water without the high accuracy ab initio data. The large consistency between the CR-CC(2,3)+Q(b) and MRCI(Q) results in these intermediate regions of the water potential suggest that we should be able to use the CR-CC(2,3)+Q(b) approach and, once developed, the CR-CC(2,4) approach to provide the necessary information to improve the ES and other existing global potential functions.

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